Unconventional Magnetic Correlations in DyB_2C and HoB_2C

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Layered borocarbides RB_2C (R = Dy, Ho, and Er) have been studied by powder neutron diffraction at 2–30 K. ErB_2C has two-sublattice antiferromagnetic order below $T_N = 16.3$ K, but DyB_2C and HoB_2C show a coexistence of a conventional canted $\mathbf{k} = (000)$ ferromagnetic structure and unconventional magnetic correlations. The $\mathbf{k} = (000)$ phase orders at $T_c = 8.5$ K (DyB_2C) and 7.1 K (HoB_2C), but low-Q diffraction peaks from the unconventional correlations appear above T_c with different critical temperatures for different peaks: at 8, 10.5, and 15.7 K for HoB_2C. This scattering is fitted as diffraction from a Warren-type random magnetic layer lattice and may result from quadrupolar interactions between R^{3+} spins.

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Layered rare earth borocarbides are of interest for their low temperature electronic and magnetic properties. They are generally metallic and contain layers of planar, π-bonded borocarbide layers sandwiching R^{3+} cations that have localized $4f^n$ configurations. The RB_2C_2 family was studied extensively following the discovery of antiferroquadrupolar order at $T_Q = 24.7$ K in DyB_2C_2 [1,2].

A variety of magnetic phases including spin density wave structures are found in other RB_2C_2 [3–6]. The magnetic properties of the related RB_2C family of borocarbides (R = Sc, Y, and Tb-Lu) [7–9] have not been reported. These contain planar B_2C sheets of fused 4- and 7-membered rings, with the R cations located between the 7-membered rings of successive sheets (Fig. 1). It was originally reported that successive B_2C layers were rotated by 90° giving a tetragonal structure [1–3]; however, a reinvestigation of HoB_2C [10] has shown that the B_2C layers are stacked directly above each other leading to an orthorhombic structure (space group $Pbam$), which may have a slight monoclinic distortion to $P112/m$ symmetry, although this has not yet been proven. Despite the lowering of symmetry, the R cation array remains pseudotetragonal. We report here a low temperature neutron powder diffraction study of DyB_2C, HoB_2C, and ErB_2C which has revealed unconventional magnetic correlations in the first two materials.

Polycrystalline samples of RB_2C (R = Dy, Ho, Er) were prepared by arc melting 7 g pellets of the powdered elements (99.9% R, submicron 99.999% graphite, and 99.1% boron-11 isotope to minimize neutron absorption) on a water cooled copper hearth in an argon atmosphere. The samples were remelted several times to improve homogeneity. Neutron scattering experiments between 4 and 30 K were performed on diffractometer D1B at the Institute Laue-Langevin, Grenoble, France. The samples were placed in a sealed vanadium can within a He cryostat. An annular sample of DyB_2C was used in view of the large absorption cross section of natural Dy. Diffraction

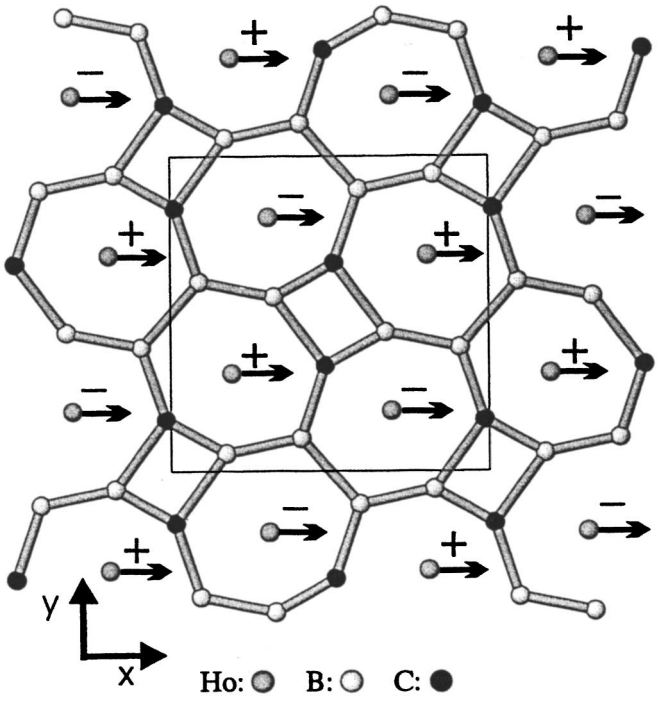

FIG. 1. [001] projection of the HoB_2C structure. The ferromagnetic x components of the $\mathbf{k} = (000)$ magnetic structure are shown and the antiferromagnetic z components are indicated by +, −.

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profiles were recorded over 2°–82° 2θ at a neutron wavelength of 2.52 Å, giving a wave vector range of $Q = 0.1$–3.3 Å^{-1}. Rietveld analyses were carried out using the FULLPROF program [11]. Additional, time-of-flight neutron spectra of HoB_2C were recorded on the LOQ instrument at the ISIS spallation source, U.K.

The neutron profile of ErB_2C was fitted by the monoclinic HoB_2C structural model [4] [$a = 6.736(6)$, $b = 6.757(5)$, $c = 3.636(9)$ Å, and $\gamma = 90.12(8)°$ at 18.5 K]. A single antiferromagnetic ordering transition is observed at $T_N = 16.3$ K. The magnetic peaks are all indexed by the $\mathbf{k} = (000)$ propagation vector, and the intensities at 4 K were fitted by a collinear, two-sublattice antiferromagnetic model, with Er moments of $9.06(5)\mu_B$ in the c direction at (± 0.31, ± 0.81, 0.5) antiparallel to those at (± 0.19, ± 0.31, 0.5).

HoB_2C [$a = 6.760(1)$, $b = 6.761(1)$, $c = 3.6901(2)$ Å, and $\gamma = 90.16(2)°$ at 30 K] shows an unusual evolution of magnetic neutron scattering at low temperatures (Fig. 2). Between 16 and 8 K, three peaks appear at low Q, all with different critical temperatures (Fig. 3). Sharp, resolution-limited peaks occur at $d = 11.43$ Å [$T_c = 15.7(2)$ K] and at $d = 22.78$ Å [$T_c = 10.5(3)$ K], and a broad, asymmetric peak appears at $d = 35.8$ Å ($T_c = 8$ K). The former two peak intensities follow typical critical behavior below their T_c's, with exponents of $\beta = 0.32(4)$ and 0.33(7), respectively, whereas the intensity evolution of the broad 35.8 Å peak (Fig. 3) evidences strong critical fluctuations above the T_c. To verify that the unusual low-Q peaks are elastically scattered and are intrinsic to the sample, additional time-of-flight measurements at 2–20 K [Fig. 2(b)] were made on the LOQ spectrometer. The same low-Q peaks are evident in these spectra, with the same temperature variations as above, although the lower instrumental resolution prevents the 36 Å peak from being resolved from small angle scattering of the incident beam.

A conventional magnetic order transition occurs at $T_c = 7$ K in HoB_2C, with many magnetic diffraction peaks indexed by propagation vector $\mathbf{k} = (000)$ appearing simultaneously at longer Q. These magnetic diffraction intensities are fitted by a canted spin model (Fig. 1), in which the z spin components have the same antiparallel arrangement as those in ErB_2C, but with additional ferromagnetic components of $2.4(3)\mu_B$ per Ho^{3+} present in the xy plane. The resultant moments are canted by 56.1(9)° from the c direction and have a magnitude of $2.94(2)\mu_B$ at 4 K. This is considerably less than expected for Ho^{3+}, for example, in HoB_2C_2 ($T_c = 5.8$ K) the ordered 4 K moment is $7.8\mu_B$ [3]. The temperature variation of the (110) magnetic intensity (Fig. 3) is fitted with critical exponent $\beta = 0.36(4)$.

The low Ho moment in the $\mathbf{k} = (000)$ magnetic phase and the absence of any structural distortions on cooling indicate that the additional low-Q scattering arising between 16 and 8 K is due to additional magnetic order [12]. This scattering is not typical of spin wave or other magnetic superstructures which are common in rare earth

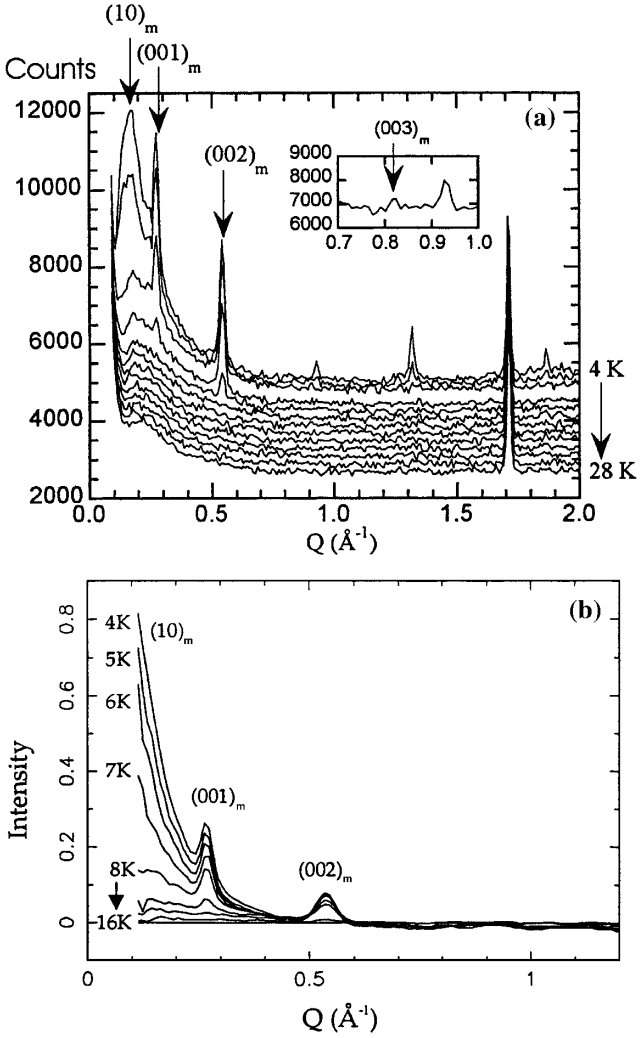

FIG. 2. Neutron diffraction data for HoB_2C. (a) Constant wavelength D1B profiles between 4 and 28 K in 2 K intervals, successively offset by 200 counts. Magnetic random layer lattice peaks are indicated and the inset shows the weak $(003)_m$ peak in a longer scan at 4 K. (b) Time-of-flight LOQ data at 4, 5, 6, 7, 8, 10, 12, and 16 K; the 20 K spectrum has been subtracted from the spectra shown.

metals and their compounds, but can be described using the random layer lattice theory of Warren [13]. For a lattice of internally ordered layers stacked regularly in the c direction, but with random layer translations and rotations in the ab plane, only sharp (00l) and broad, asymmetric, two-dimensional (hk) diffraction peaks are observed, and no general (hkl) reflections result. The low-Q region of the difference between 4 and 30 K powder neutron diffraction spectra of HoB_2C was fitted by peaks of arbitrary intensity within the Warren model. The 22.78 and 11.43 Å peaks were assigned as $(001)_m$ and $(002)_m$ (the m subscript refers to the magnetic random layer lattice throughout) and were fitted using a Gaussian peak shape function. The indexation was corroborated by observation of a very weak $(003)_m$ peak at $d = 7.7$ Å [see Fig. 2(a) inset]. The asymmetric 35.8 Å peak was

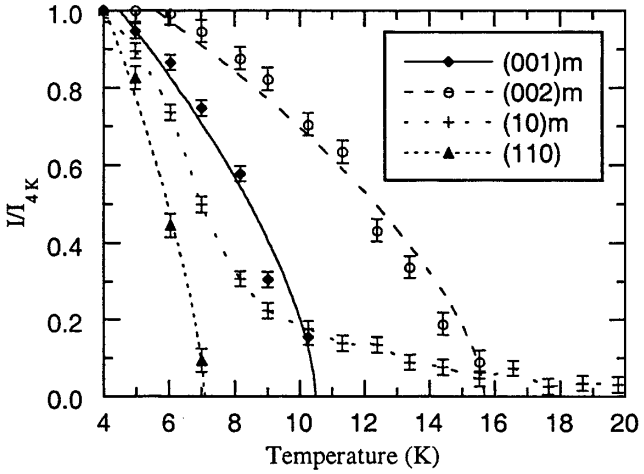

FIG. 3. Thermal evolution of magnetic peak intensities (normalized to 4 K values) for HoB_2C. The $(001)_m$, $(002)_m$, and $\mathbf{k} = (000)$ phase (110) intensities, shown below their T_c's, are fitted as $I = I_0(1 - T/T_c)^{2\beta}$. The $(10)_m$ intensities are shown over the entire temperature range with an empirical curve.

assigned as $(10)_m$ and was fitted by the Warren function [13]. Residual intensity at $d \approx 25$ Å was fitted by a second Warren peak at the tetragonal $(11)_m$ position. The good overall fit (Fig. 4) shows that the low-Q magnetic scattering features for HoB_2C are consistent with a magnetic random layer lattice, with tetragonal cell parameters $a_m = 40(1)$ Å and $c_m = 22.9(1)$ Å. The correlation length in the ab plane is estimated to be 90(3) Å $\approx 2.3a_m$ from the $(10)_m$ peak width. The correlation length in the c direction is > 1000 Å as the $(001)_m$ reflection widths are instrumentally limited.

Magnetic susceptibility data for HoB_2C (Fig. 5) show Curie-Weiss behavior at high temperatures and the effective paramagnetic moment of $10.86\mu_B$ is close to the free ion value of $10.60\mu_B$ for $4f^{10}$ Ho^{3+}. Divergence of zero-field-cooled (ZFC) and field-cooled (FC) susceptibilities

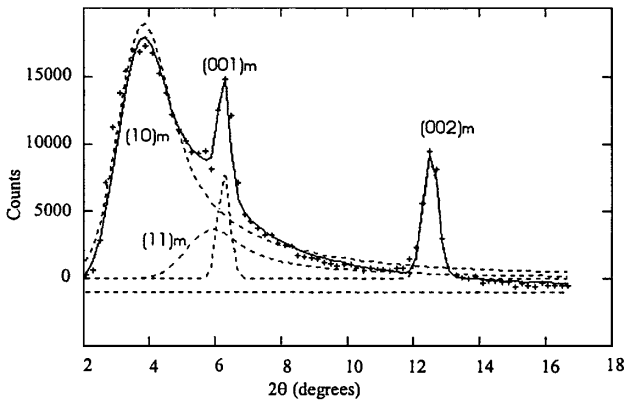

FIG. 4. Fit to the low-Q difference between 4 and 30 K D1B neutron diffraction patterns of HoB_2C. Observed (+) and calculated (full line) profile intensities and individual peak contributions from the magnetic random layer lattice (broken lines) are shown.

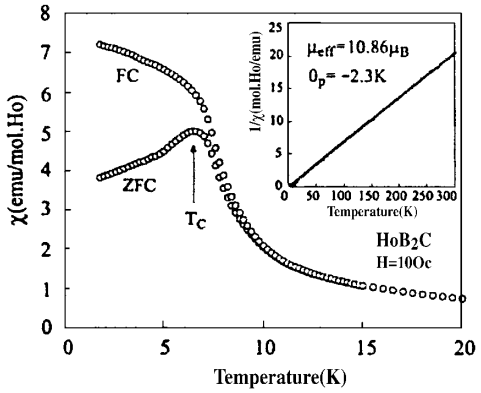

FIG. 5. Low temperature ZFC and FC magnetic susceptibilities of HoB_2C. The inset shows the Curie-Weiss fit to the inverse susceptibility.

is as expected for the 7 K canted ferromagnetic ordering transition. No magnetization anomalies are evident in the 8–16 K region.

DyB_2C has cell parameters $a = 6.764(3)$, $b = 6.763(5)$, $c = 3.704(2)$ Å, and $\gamma = 90.25(5)°$ at 30 K. The low temperature scattering (Fig. 6) contains similar peaks to those of HoB_2C, although neutron absorption by Dy leads to poorer counting statistics and a relatively intense background feature at $Q = 0.26$ Å^{-1}. This overlaps the $(10)_m$, $(11)_m$, and $(001)_m$ peaks, making their temperature variations uncertain. However, the sharp $(002)_m$ peak at $d = 11.51$ Å is clearly resolved and has $T_c = 21.6$ K. The low Q difference between scattering at 1.5 and 30 K (Fig. 6 inset) is fitted by the same envelope of asymmetric Warren $(10)_m$ and $(11)_m$ peaks and sharp $(001)_m$ and $(002)_m$ reflections as for HoB_2C (Fig. 4). The random magnetic layer lattice has tetragonal cell parameters $a_m = 42(1)$ and $c_m = 23.0(1)$ Å. The conventional $\mathbf{k} = (000)$ magnetic phase orders at $T_c = 8.5$ K and the diffraction

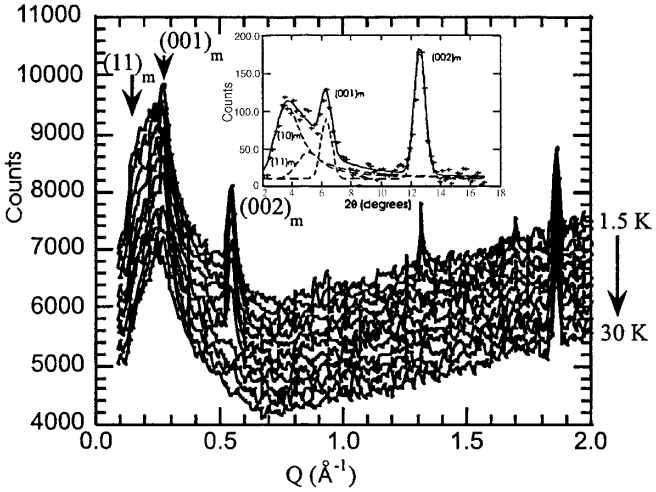

FIG. 6. D1B neutron diffraction patterns for DyB_2C between 1.5 and 30 K. The inset shows the fit to the low-Q difference between 1.5 and 30 K data, as in Fig. 4.

peaks were fitted by the same canted spin model as for HoB_2C. The refined tilt angle from c is 47(5)° and the ordered Dy moment of $3.3(3)\mu_B$ at 4 K is much lower than the value of $8.3\mu_B$ in DyB_2C_2 [3]. Magnetization data for DyB_2C are similar to those for HoB_2C; the paramagnetic effective Dy moment is $10.63\mu_B$ and the Curie transition is at 8.5 K with divergence of ZFC and FC susceptibilities. Further magnetization and specific heat results for HoB_2C and DyB_2C will be published elsewhere.

The scattering angles and peak shapes of the low-Q magnetic scattering for HoB_2C and DyB_2C are consistent with a Warren-type magnetic random layer lattice, although the crystal structures of the RB_2C samples are ordered in three dimensions. The low-Q scattering is quite different from that of the modulated spin structures that are common in rare earth compounds, e.g., in HoB_2C_2 [3,5], which give rise to magnetic satellites of the nuclear Bragg (hkl) reflections. The scattering from the HoB_2C and DyB_2C magnetic random layer phases is observed only for $Q < 0.9$ Å^{-1}, showing the ordered moments to be small, whereas the $\mathbf{k} = (000)$ magnetic and nuclear diffraction peaks are found at higher Q. The lack of any satellite peaks prevents the relative orientation of the nuclear and random layer magnetic cell vectors from being determined in these powder experiments. However, it is likely that the stacking axis of the random magnetic layers c_m coincides with the c vector of the pseudotetragonal layered crystal structure. The two periodicities are not commensurate: $c_m = 6.21(3)c$ for HoB_2C. The same factor of ~6 exists between a_m and the a or b nuclear cell parameters.

Another unconventional feature of the low-Q scattering is that the magnetic random layer peaks appear at different temperatures, so they do not necessarily belong to a single magnetic phase. Whether the diffracted intensities are consistent with a single magnetic model from which structure factors could be calculated is not yet clear. The $(002)_m$ and $(001)_m$ intensities, and the (110) peak of the conventional $\mathbf{k} = (000)$ magnetic phase, all have exponents $\beta \approx 0.33$ for HoB_2C, which is typical for long range magnetic ordering transitions. The strong critical scattering observed above $T_c \approx 8$ K is consistent with the two-dimensional nature of the $(10)_m$ reflection.

The origin and static or dynamic nature of the unconventional magnetic correlations are not yet known, but as RB_2C_2 with R = Ho and Dy both have antiferroquadrupolar ordering transitions (T_Q), it seems likely that the unconventional magnetism of the RB_2C analogs is also related to ordering of $4f^n$ quadrupoles or multipoles. The ordering temperatures for DyB_2C_2 are higher than for HoB_2C_2 although their magnetic ordering sequences differ; DyB_2C_2 has $T_Q = 24$ K, above the only magnetic phase transition at 18 K, whereas HoB_2C_2 has a spin density wave magnetic transition at 5.8 K and a second magnetic transition at $T_Q = 5.0$ K. The RB_2C phases are more comparable: T_c for $(002)_m = 22$ K for DyB_2C and 16 K for HoB_2C, and the respective T_c's for their $\mathbf{k} = (000)$ phases are 8.5 and 7.1 K.

In conclusion, both HoB_2C and DyB_2C display coexistence of a canted ferromagnetic $\mathbf{k} = (000)$ spin structure and unconventional magnetic correlations that give rise to low-Q elastic neutron scattering. The scattering angles and shapes of the latter diffraction peaks are consistent with the Warren model of a random layer lattice. However, the peaks appear at different critical temperatures, above that of the $\mathbf{k} = (000)$ phase. The competing ground states result from complex spin-spin interactions that probably involve quadrupoles or higher multipoles of the $4f^n$ configurations, coupled to the lattice degrees of freedom, and further measurements and neutron scattering experiments, in particular, from single crystals, will be needed to elucidate this unusual physics.

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